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ELECTRICAL CONDUCTION IN DILUTE AMALGAMS

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The modern theory of electrical conduction in metals, according to which the metal is dissociated to give a positive ion of low mobility, which is characteristic of the metal, and a negative carrier of high mobility, which is common to all metals and presumably to be identified with the electron, has given rise to certain misgivings, despite the complete analogy between this theory and the accepted theory of electrolytic dissociation. It is true that in the case of solid metals the crystal-line forces, which lead to the formation of the various components of the metal into symmetrical space-lattices, produce conditions which have no counterpart in liquid electrolytes, but in the case of a liquid metal like mercury we must assume that it differs from any electrolyte—we are tempted to say from any other electrolyte—only in as far as one of its ions has properties which differ very greatly in degree, but probably not in kind, from the properties of other ions. If therefore we should ultimately find that the Arrhenius theory of ionization is not applicable to a liquid metal we should be inclined to believe that it is not completely valid in the case of electrolytes.

This theory of electrolytic dissociation, which was originally proposed to explain the properties of aqueous salt solutions, has since been successfully applied without essential modification to many types of non-aqueous solution. Moreover the extremely important work of Kraus,¹ which unfortunately has not yet been published in full, demonstrates the applicability of the same theory to solutions of metals in non-metallic solvents. Thus, when metallic sodium dissolves in liquid ammonia, he shows conclusively that it dissociates into sodium ions and into electrons which, like other ions, are to a considerable extent combined with the molecules of the solvent.

Since therefore the theory of ionization has been successfully applied to electrolytes and to solutions of metals in electrolytes, it seems desirable to attempt a further extension of these ideas by several methods to solutions of metals in metallic solvents, in particular to solutions of the alkali metals in liquid mercury, and thus eventually to pure mercury itself. It has been shown by Lewis, Adams, and Lanman² that the transference of matter with the electric current, which had previously been regarded as a distinguishing characteristic of electrolytic conductors, can be detected and measured in sodium and potassium amal-

gams. It is to be hoped that further knowledge of the transference numbers so obtained, together with accurate information concerning the electrical conductivity of amalgams, may furnish important evidence as to the nature of electrical conduction in dilute amalgams and in pure mercury.

Important investigations of the conductivity of amalgams and liquid alloys have been conducted by Bornemann and his collaborators,³ but they have confined their studies to high concentrations. If from transference number and conductivity we propose to obtain information concerning the nature of the carriers in the amalgams and in pure mercury, analogous to that which has been derived from a similar study of aqueous solutions, we may expect the most significant results from an investigation of dilute amalgams, ranging from zero to one atom per cent. We shall describe in this paper the results of an investigation of the conductivity of dilute amalgams of sodium, potassium, and lithium.

Since the conductivity of these amalgams differs but little from that of pure mercury, the difference itself can be determined with accuracy only by methods of the highest precision. By means of a simple potentiometer method it was found possible to compare the conductivity of an amalgam with that of pure mercury with an accuracy of two or three parts in one hundred thousand. (Full details of the potentiometer method, together with the method of preparing, transferring and analyzing the amalgams, are contained in a paper which will shortly be offered for publication in the *Journal of the American Chemical Society*.)

The experimental results are given in the three following tables, in each of which the first column gives the atom per cent of alkali metal, and the second the specific resistance divided by that of pure mercury at the same temperature. The measurements were all made at about 20°C.

TABLE I
LITHIUM AMALGAM

ATOM PER CENT	RESIST- ANCE RE- FERRED TO MERCURY
0.03269	0.999468
0.09988	0.998280
0.3080	0.994006
0.4844	0.990105
0.7103	0.985603
0.8221	0.983097

TABLE II
SODIUM AMALGAM

ATOM PER CENT	RESIST- ANCE RE- FERRED TO MERCURY
0.09325	1.00071
0.2905	1.00204
0.3851	1.00274
0.8646	1.00535
1.197	1.00657
1.670	1.00800
2.113	1.00867
2.409	1.00893
2.644	1.00824
3.661	1.00657
4.916	1.00621

TABLE III
POTASSIUM AMALGAM

ATOM PER CENT	RESIST- ANCE RE- FERRED TO MERCURY
0.05831	1.00220
0.1791	1.00574
0.4068	1.01767
0.5590	1.02623
0.6502	1.03032
0.8777	1.04147
1.186	1.05341

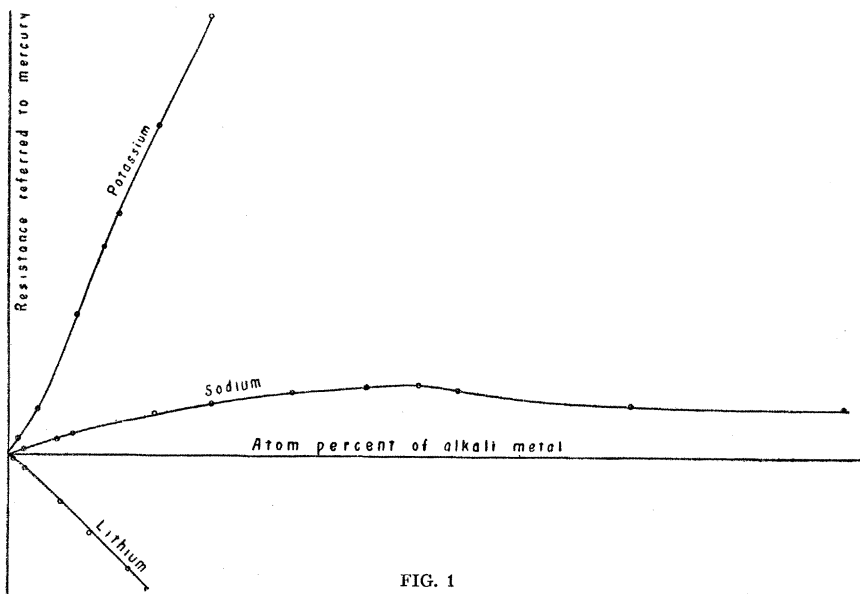


FIG. 1

The extraordinary difference between the three types of amalgam is shown in figure 1, from which it will be seen that a small addition of potassium increases the resistance of mercury, an equivalent amount of sodium produces a less increase in the resistance, while the addition of lithium diminishes the resistance.

It might have been expected, at first sight at least, that in accordance with the theory of electrolytic dissociation the strongly electropositive alkali metals would, owing to a greater dissociation, increase the conductivity of mercury. But when we consider the well substantiated fact that all these metals are, when dissolved in mercury, combined with the solvent to form hydrargyrites of greater or less complexity, the results cannot be considered to disprove this theory. Nevertheless it is important to observe that in interpreting the conductivity and transference number of dilute amalgams, the generalizations which can be drawn and the analogies which suggest themselves are of a very different character from those which have been found useful in the interpretation of the phenomena of aqueous solutions.

Thus in the paper of Lewis, Adams, and Lanman it has been shown that, contrary to expectation, the strongly electropositive metals sodium and potassium, when dissolved in mercury, wander in the direction not of the positive but of the negative current. They show further that this phenomenon is closely correlated with the increase in resistance produced in mercury by the solution of these metals; for if the in-

creased resistance be ascribed to a greater resistance to the motion of the electron in those regions of the mercury which contain particles of the dissolved metal, these particles or regions, according to the law of action and reaction, will be impelled in the direction in which the electrons are moving. This explanation is borne out by the fact that potassium, which produces a greater increase in the resistance of mercury than an equivalent amount of sodium, is also transferred to a greater extent in the direction of the negative current.

We may also suggest here another relationship of considerable interest. Attention has been called by Kraus⁴ to the very large influence upon the conductivity of liquid mercury of a change of volume through pressure. Now it has been shown by Maey⁵ that the addition of the alkali metals produces a very considerable change in the volume of mercury. This change in volume follows the same order as the electrical resistance of the amalgams given in the preceding tables. It is interesting therefore to see how the resistance of mercury would change upon the addition of the three alkali metals, if this addition were made, not at constant pressure, but with such change of pressure as would keep constant the average atomic volume, that is, the volume occupied by 1 gram of solvent and solute together.

If R is the resistance of pure mercury, V and V' the atomic volumes respectively of pure mercury and of amalgams, P the pressure in kilograms per square centimeter, and N the atomic fraction of the dissolved metal, then, according to the measurements of Bridgman,⁶ $d\ln R/dP = -3.34 \times 10^{-5}$, while from the measurements of Richards, of Buchanan, and of Bridgman,⁷ $d\ln V/dP = -3.8 \times 10^{-6}$. Hence $d\ln R/d\ln V = 8.79$. In Table IV the second column gives the value of $d\ln V'/dN$ calculated from the work of Maey, and the third column the values of $d\ln R/dN$, which are obtained from the second column through multiplication by 8.79. These figures therefore show the change in the resistance of mercury which would be produced by the three metals, assuming that the effect of the dissolved metal is due solely to the accompanying volume change. The fourth column gives the values of $d\ln R/dN$ obtained directly from our measurements, by finding the slope of the resistance curve at $N = 0$. These figures will vary somewhat according to the relative weight given to the measurements at the lowest concentration. The fifth column gives the values of $(d\ln R/dN)_{V'}$, namely, the fractional change in the resistance per gram-atom of dissolved metal when the average atomic volume is kept constant. These figures are obtained by subtracting the second column from the third.

TABLE IV

	$\frac{d \ln V'}{dN}$	$\frac{d \ln R}{dN}$ (calc.)	$\frac{d \ln R}{dN}$ (obs.)	$\left(\frac{d \ln R}{dN}\right)_{V'}$
Lithium.....	-0.534	-4.70	-0.82	+3.88
Sodium.....	-0.014	-0.12	+0.92	+1.04
Potassium.....	+0.643	+5.66	+2.73	-2.93

It is evident that when added at constant atomic volume lithium would increase and potassium decrease the resistance of mercury, the very reverse of that which happens at constant pressure. The parallelism between the figures of the second and the third columns is striking; we need not, however, consider the change in volume and the change in resistance to be directly related as cause to effect, but rather we shall regard them as concomitant effects of some condition in the immediate neighborhood of the dissolved particles, a condition which probably is closely connected with what is known as the solvation of the dissolved metal. The amount of this solvation or combination with the solvent undoubtedly increases in the same order as the electrical resistance, being least in the case of lithium and greatest in the case of potassium. Thus, to cite one of the most direct pieces of evidence, it is shown by Lewis and Keyes⁸ that the heats of solution in mercury of lithium, sodium, and potassium are respectively 19,600, 19,800 and 26,000 calories.

In drawing attention to the difference between the phenomenon of conductivity in dilute amalgams and in dilute electrolytic solutions, it is only just to remark that, since we are considering solutions in a solvent which is itself a good conductor, the case is not entirely analogous to that of salts dissolved in a poor conductor like water, but rather to a solution of a salt in another molten salt, a system which has not as yet been intensively studied.

¹ Kraus, *J. Amer. Chem. Soc.*, **29**, 1557 (1907); **30**, 653 (1908); **30**, 1197 (1908); **30**, 1323 (1908); **36**, 864 (1914).

² Lewis, Adams, and Lanman, *J. Amer. Chem. Soc.*, **37**, 2656 (1915).

³ Bornemann, *Metallurgie*, **7**, 730 (1910); **9**, 473 (1912).

⁴ Kraus, *Physic. Rev.*, Ser. 2, **4**, 159 (1914).

⁵ Macy, *Zs. physik. Chem.*, **29**, 119 (1899).

⁶ Bridgman, *Proc. Amer. Acad. Arts Sci.*, **44**, 221 (1909).

⁷ Landolt, Börnstein, and Roth, *Tabellen*.

⁸ Lewis and Keyes, *J. Amer. Chem. Soc.*, **35**, 340 (1913).